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Thesis

QUALITATIVE MICROANALYSIS

by

Kathleen Ellen Shreeve

(A.B., Boston University, 1932)

submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

1933

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Object of Thesis

Microchemistry has only recently demanded our attention. It was in quantitative analysis that micro methods first made an appearance. The work of this branch has been well established. Qualitative analysis next felt the influence of micro methods. While considerable work has been done in this field, there are still many opportunities for improvements in both the technique and the plan of analysis. The work in qualitative analysis is not yet on a level with that in quantitative analysis. At the present time we find that efforts are being made to make practical the application of micro methods in organic chemistry.

The object of this thesis is to set forth experimental work which I have done in qualitative microanalysis. A scheme of analysis has already been devised by Carl Engelder. I have taken Engelder's rough notes as a basis for procedure and tried to work out, and either verify or improve, the method of analysis. I have indicated the more important changes or additions made in Engelder's scheme, by underlining and by parenthetical explanation. In general, the same tests were used which were suggested by Engelder; except that several confirmatory tests were omitted. These omissions were made either because the test was not good (and where there was already one good test, it only caused confusion), or because the reagents needed for these tests were not available. The changes made are mostly in the quantities used, the form of

Object of Thesis

substance used (solution or powder) and the apparatus and general technique. Engelder only mentions the apparatus as it is used, and fails to give any description of it, to suggest how it can be made, or to explain how it is to be used. In this thesis I have included a section on apparatus and technique which precedes the formal scheme of analysis, and which was entirely omitted by Engelder.

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Introduction

Microanalysis is primarily a technique. For qualitative analysis the scheme is the same, in general, as that followed in the ordinary course using macro methods. The difference lies in the amount of substance used. This in turn necessitates different apparatus and technique, and in a few cases a different test for an element or radical. Microanalysis can be done successfully, as in this plan, without a microscope. However a microscope may be used profitably for the study of crystal structure as a means of identifying certain compounds. A spectroscope may also be used to advantage for the detection of elements in very small amounts.

There are many differences between macro and micro methods. Perhaps some idea of the nature of microanalysis may be gained by noting these differences. In macro work the solutions are made up so as to contain 10 mg. per cc. of any one cation or anion. Microanalysis employs solutions containing only 1 mg. per cc. of a particular cation or anion. There is a change in quantity as well as concentration. In micro work the analysis is begun with only 2 or 3 cc. of the solution, and the tests for individual members are carried out on 1 or 2 drops only. A very marked change in technique is found in the use of the centrifuge for the separation of precipitate and solution, replacing the old method of filtration. As a result of this, centrifuge tubes replace the ordinary test tubes. Because reagents are used by the drop rather than by the cubic

Introduction

centimeter, the pipette plays an important role as a piece of apparatus. There must be in fact many pipettes. The tests for the individual cation or anion are generally made on a spot plate or a glass slide. Other pieces of apparatus which may be very useful, although not absolutely necessary, are the micro burner and micro crucible, evaporating dish or casserole.

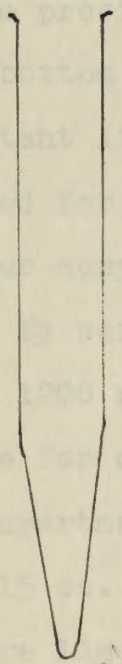


Figure 2

The 3cc. Centrifuge Tube

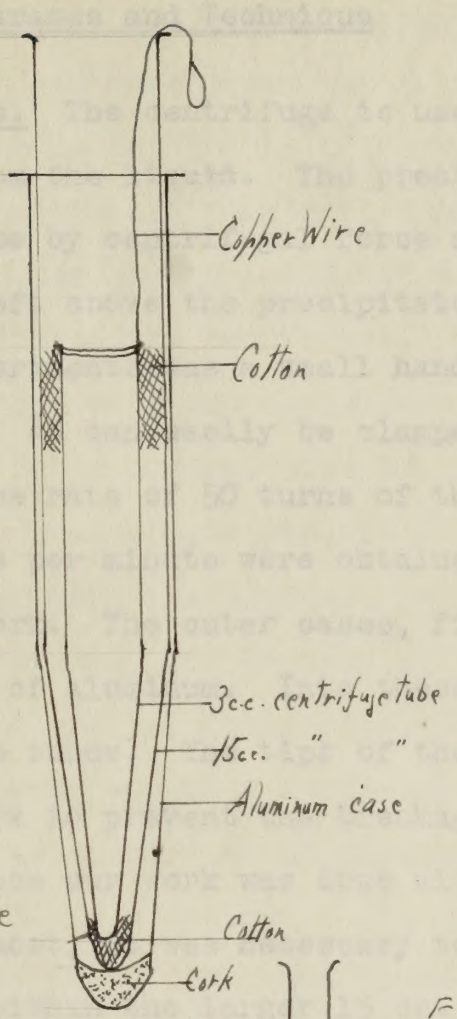


Figure 1

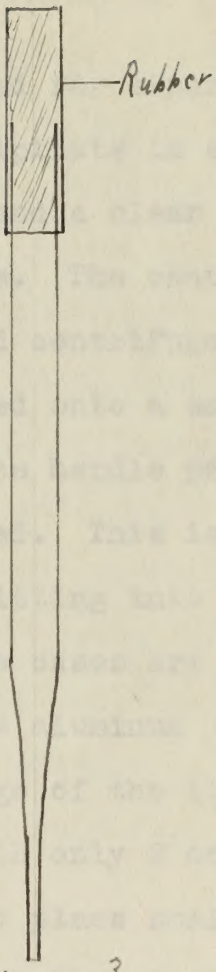


Figure 3

The Pipette

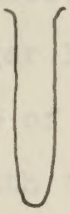


Figure 5

1c.c. Crucible

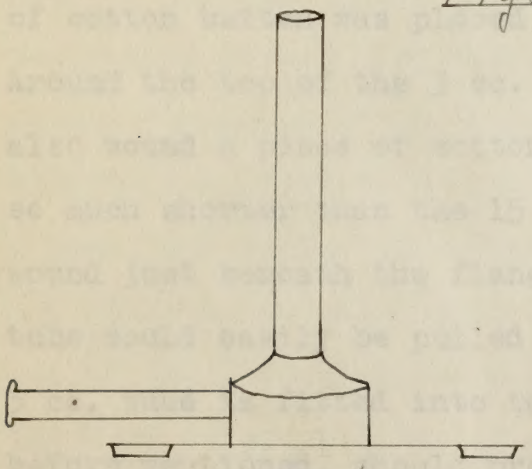
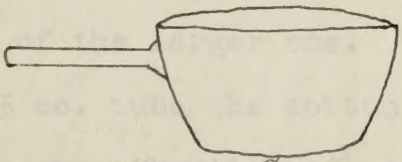


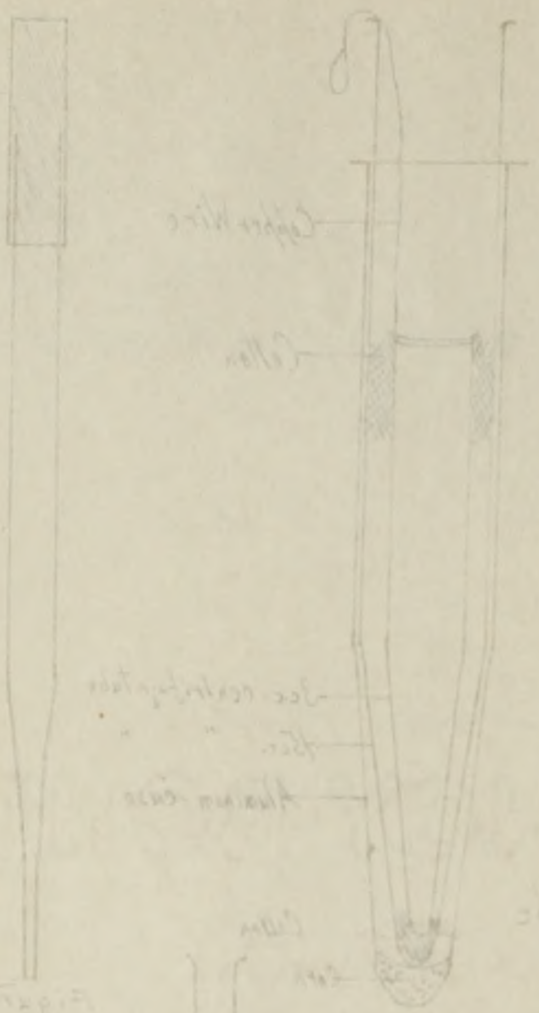
Figure 4

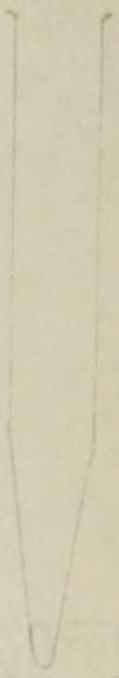
The Micro Burner

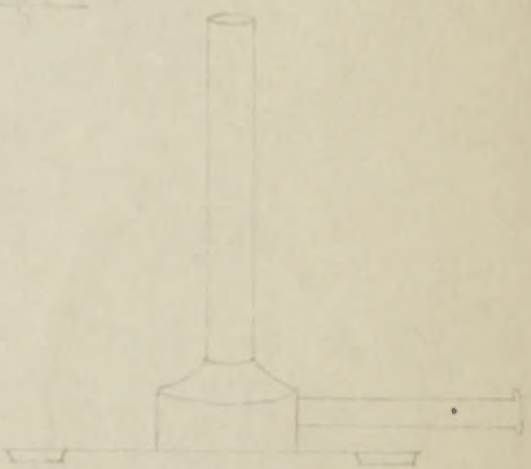


3c.c. Casserole

(Drawn to scale - actual size)







Apparatus and Technique

The Centrifuge. The centrifuge is used for separating the precipitate from the liquid. The precipitate is sent to the bottom of the tube by centrifugal force and a clear supernatant liquid is left above the precipitate. The centrifuge used for these experiments was a small hand centrifuge with four compartments. It can easily be clamped onto a small table. By working at the rate of 50 turns of the handle per minute, 1200 revolutions per minute were obtained. This is suitable for ordinary work. The outer cases, fitting into the four compartments, were of aluminum. Into these cases are fitted 15 cc. centrifuge tubes. The tips of the aluminum cases are lined with cork to prevent the breakage of the tips of the glass tubes. Since our work was done with only 2 or 3 cc. of solution at the most, it was necessary to place small 3 cc. centrifuge tubes within the larger 15 cc. tube. A piece of cotton batten was placed in the tip of the 15 cc. glass tube. Around the top of the 3 cc. tube beneath the flange there was also wound a piece of cotton batten. Since the 3 cc. tube was so much shorter than the 15 cc. one a piece of copper wire was wound just beneath the flange and a loop left so that the small tube could easily be pulled out of the larger one. When the 3 cc. tube is fitted into the 15 cc. tube the cotton batten, before mentioned, should prevent any vibration of glass against glass which might cause breakage. (See figure 1) Every time before centrifuging care must be taken that the centrifuge is

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balanced; that is there must be a compensating weight in the compartment opposite the one containing the solution. This is obtained by placing water in the 15 cc. tube in the opposite case. It is well to keep a small beaker of water near the centrifuge so that the water may be added to, or taken out of this tube in order to balance the centrifuge. Care should be taken that there is nothing near the centrifuge which might be struck when the machine is in motion. The length of time one must run the centrifuge for complete separation will depend on the nature of the precipitate, the coarser, heavier precipitates separating most rapidly. One minute (at 50 turns a minute) is usually sufficient for group precipitation; and for separations within the group one-half minute is often all that is needed. The centrifuge should not be stopped suddenly, but allowed to slow down of its own accord.

The Centrifuge Tubes. The centrifuge tubes were made from 10 mm. glass tubing of 10 cm. (8 in.) lengths. This was heated over a wing top burner and drawn out. The portion heated should be about 3 cm. in length, so that the tubing willprobably have to be held somewhat diagonally across the flame. The tubing after being drawn out should be cut where the diameter is about 3 to 4 mm., and then sealed. The other end of the tubing can then be cut so that the final length of the tube is about 8 cm. Finally the flange is made at the top of the tube. (See figure 2) When heating these tubes care must be taken not to get the tips too hot as they easily

crack off. A small test tube holder for these small tubes can be made by slightly bending the ends of a pair of straight forceps.

The Pipettes. The pipettes are likewise made by drawing out glass tubing, but of 6 mm. diameter, and about 10 in. lengths. Again it is well to hold the tube diagonally over the flame so as to heat a short length only. The tubing is drawn out to 1 mm. diameter. The more rapidly the tube tapers the better, for a long slowly tapering end is more easily broken. The final length of pipettes should be from 4 to 5 inches. A piece of rubber tubing about 3 cm. in length is fitted onto the end of the tube. (See figure 3) By placing the index finger over the end of the rubber and using the thumb and second finger to pinch the rubber, the pipette can easily be filled, and the solution let out drop by drop. The pipette has many uses and each student should have a good supply of them. Solutionsare placed in the centrifuge tube by means of a pipette, and all the reagents are added drop by drop from the pipette. When H_2S is to be passed into the solution, a pipette is attached to the generator in order to conduct the gas into the solution. After centrifuging, the supernatant liquid is removed by means of a pipette. However, when there are 2 or 3 cc. of liquid, it may be decanted and only the last few drops removed with the pipette. The residue is so solidly lodged in the point of the tube that it is not disturbed by decanting. After adding water or other liquid for washing the

residue, the tip of the pipette should be inserted into the tube down to the residue. Then if air is gently bubbled through the liquid by pressing the rubber tubing, the residue is disturbed and thereby thoroughly washed. It is generally recommended to stir with a platinum wire or glass rod, but neither of these seemed effective. The wire was not stiff enough and the rod was clumsy. The solution finally obtained for testing is dropped by means of a pipette onto a glass slide or a spot plate and a drop of reagent added. A pipette used for one solution should not touch a drop of another. The drop of reagent should leave the pipette just above the other drop.

The Spot Plate. As has been mentioned the spot plate finds its greatest use as a receptacle for individual tests. A drop of solution to be tested being placed in a cavity and a drop of reagent added. The spot plate is also useful as a receptacle in which to dilute reagents, to mix two or more solutions, or to make pastes.

A drop of solution can also be placed on a glass slide for testing. This has the advantage of being able to be placed over white filter paper or black glazed paper and thus providing backgrounds which show the color of solution or precipitate to the best advantage. In case crystal structure is to be observed glass slides are used for the tests and the crystals which form on the slide can then be easily seen through the microscope.

A square of black, opaque glass is also good for some tests, especially those in which a white precipitate is formed.

The Micro Burner. Small micro burners can be bought especially for this work. (See figure 4) The flame that they give is quite hot and care must be used when heating tubes. If a mouth blow pipe is attached by rubber tubing to the gas pipe a small flame can be produced which serves as a good substitute for the micro burner. The blow pipe should be clamped to a stand. It is even possible to use a good Bunsen burner, turned very low, as a source of heat.

A Test-Tube Rack. The ordinary test tube rack is too large for the small tubes used in micro work. One form of rack may be made by boring holes in a small paste board box which is fairly strong. The holes should be of different sizes to fit the different tubes.

Gas Evolution Tubes for Anion Analysis. In several of the tests for anions, a gas is evolved which has to be tested. In each case only one or two drops of solution are used so that the volume of the gas evolved is very small. Therefore the volume of air which this gas has to displace before reaching the top of the tube must of necessity be small also. The 3 cc. centrifuge tube proved to be too large. Small tubes were made by drawing out 6 mm. glass tubing until it was only 3 to 4 mm. in diameter. The tubing was cut into 3 or 4 cm. lengths, sealed at one end, and a flange made at the other end. (See figure 5)

Crucibles and Casseroles. Very small crucibles and casseroles can now be obtained for microanalysis. This apparatus is not absolutely necessary but is very useful for boiling or evaporating some solutions. The crucibles are of 1 cc. capacity and the casseroles of 3 cc. capacity.

Reagent Bottles. The reagent bottles should be of about 150 cc. capacity and provided with a stopper carrying a pipette. As before a piece of rubber tubing is placed on the end of the pipette, but for reagent bottles this is plugged with a short length of glass rodding. In this way reagents should remain clean, and no impurities should be introduced. Students must be warned not to touch this pipette to any other solutions. If the reagent is to be used several times within a short time, or if it is to be diluted or mixed with another reagent it is best to take several drops and deposit in in a cavity of the spot plate, to be used as needed.

Absolutely clean apparatus must be used. This might be said for all work in chemistry. But for microanalysis it is of especial importance because such small quantities are used, that a very slight impurity may cause considerable error. A funnel brush is good for cleaning centrifuge tubes. About 2 inches of the brush can be cut off the end so that the thicker upper part is used. A stream of water run through pipettes will generally clean them. Cleaning solution, however, will often have to be used for all apparatus.

The Cation Analysis

Group I-Pb, Ag, Hg .

Put 3 cc. of the solution containing Group I (alone or with other groups) into a centrifuge tube. Test the solution with red litmus to see if it is basic. If basic, bring to neutrality by adding conc. HCl drop by drop from a pipette. Then add a drop more of conc. HCl which will cause the members of Group I to be precipitated as chlorides. Centrifuge. Test for complete precipitation by adding another drop of conc. HCl. If more precipitate is formed centrifuge again. After complete precipitation decant the supernatant liquid and pipette off the last few drops. This liquid is saved if other groups are to be tested for; otherwise it is discarded. Any material to be saved for later should be placed in a tube, stoppered and plainly labelled.

Lead: To the residue of chlorides add 2 drops of water, stir and centrifuge. If lead is present, some will be dissolved by the water. Place a drop of the liquid on a glass slide, add to this a drop of potassium chromate (K_2CrO_4). The formation of a yellow precipitate ($PbCrO_4$) is a test for lead. Discard any supernatant liquid remaining in the tube. Then add 2 drops of water, stir and warm gently. Centrifuge, and test the liquid with potassium chromate as before. A yellow precipitate confirms the presence of lead. (However if lead is present in very small amounts the cold water may dissolve out most of the $PbCl_2$ so that this second test with hot water is

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not as good as the first.) Discard the rest of the supernatant liquid, and then wash the residue with 3-4 drop portions of hot water until no test for lead is obtained with the potassium chromate. (A test using H_2O_2, NH_4OH and tetramethyl-diamino-diphenyl-methane was omitted.)

Silver: After the lead has been removed add 3 drops of dilute NH_4OH to the residue. A blackening of the residue at this point indicates mercury. Warm the solution and centrifuge. Place a drop of the supernatant liquid on a glass slide and add a drop of conc. HNO_3. (Test for acidity is omitted as unnecessary.) The formation of a white precipitate (AgCl) is a test for silver. Discard the rest of the supernatant liquid. (Engelder used 1-2 drops of conc. NH_4OH for dissolving the AgCl. However when this was used, a white precipitate formed in the drop of supernatant liquid, placed on a glass slide, before any HNO_3 was added. This was due presumably to the rapid evaporation of conc. NH_4OH. Therefore dilute NH_4OH is better.) (A test with KCN, rhodamine, and HNO_3 is omitted.)

Mercury: To the black residue which remains after the extraction of silver chloride, add 1 drop of conc. HNO_3 and 3 drops of conc. HCl--aqua regia. (This is used throughout the analysis in place of a crystal of $KClO_3$ and a drop of conc. HCl.) Heat gently until all the chlorine is driven off. It was found that the best results are obtained by heating this solution in a small micro crucible if these are available. In this way the chlorine escapes more easily and rapidly. If the

solution goes almost to dryness add 2 or 3 drops of water to make up the volume again.

If the crucibles are not available it helps if a pipette is inserted into the centrifuge tube, but not into the liquid, and the rubber at the end of it compressed so that some air is driven out of the tube. This can be repeated several times.

The chlorine will have been all evolved when the solution is no longer yellow or when moist potassium iodide starch paper does not turn blue when held in the fumes. When the chlorine is removed, place a drop of the solution on a slide and add 1 or 2 drops of stannous chloride ($SnCl_2$). The formation of a grey precipitate turning black (HgCl--Hg) shows that mercury is present.

A confirmatory test for mercury is obtained by adding to a drop of solution a little powdered Na_2CO_3 and a drop of diphenylcarbazide solution. A violet to blue color is a test for mercury. (This differs from Engelder's test in that he uses 0.2 N HNO_3 with the diphenylcarbazide and carries out the test on spot paper. The solution of diphenylcarbazide here used is not the same as that used by Engelder--see list of reagents.)

Group II- Hg , Pb, Bi, Cu, Cd, As, Sb, Sr.

The solution may be the liquid saved after the removal of Group I, or a solution of Group II alone. In either case make neutral by adding conc. NH_4OH drop by drop and testing with litmus paper. Then add 1 drop of conc. HCl. (Omitted test for acidity with methyl orange.) Warm the solution and pass in H_2S for ½ minute. (Engelder says one minute but this always gives an excess of H_2S.) Members of Group II are precipitated as sulfides. Centrifuge the solution and again pass in H_2S for a few seconds to test for complete precipitation. After complete precipitation, centrifuge. If the supernatant liquid remains turbid add 1 drop of a saturated NH_4NO_3 solution and again centrifuge. (Not mentioned by Engelder.) If Group II only is to analyzed for, discard the supernatant liquid. If Groups III, IV, and V are to be analyzed remove the supernatant liquid to a micro casserole and boil to remove the H_2S. This will be all removed when there is no longer any odor of H_2S, or when moist lead acetate paper does not turn black when held in the fumes. If there is no micro casserole the solution can be boiled in the centrifuge tube and the H_2S can be blown out using the pipette.as in the case when Cl_2 was blown out of the tube containing the mercury solution (Page 13). In either case save the solution in a stoppered, labelled tube.

Add to the residue of Group II sulfides 3 drops of water and 2 drops of NH_4NO_3, heat gently, centrifuge, and add

the supernatant liquid to the liquid removed before. Repeat this washing with water and NH_4NO_3, discarding the washings, until the washing is only slightly acid.

To the residue of washed sulfides add 5 drops of saturated Na_2S solution (rather than 5-10 drops). Stir and warm for one minute. Centrifuge and remove the supernatant liquid to another tube. Repeat using 2 drops of Na_2S and 2 drops of water. Centrifuge and add the liquid to that removed before. Repeat this treatment with Na_2S and water, but discarding the liquid until the supernatant liquid when tested with dilute HCl gives no colored precipitate. A white precipitate is due to sulfur. The Na_2S dissolves the Hg, As, Sb and Sn sulfides forming Division B. The residue consists of Hg, Pb, Bi, Cu and Cd sulfides, Division A.

Division A. The residue is washed with warm water and NH_4NO_3 solution, centrifuging and discarding the supernatant liquid until the washing is slightly basic. One cc. portions of water can be used for washing since the residue is strongly basic. After washing add 3 drops of dilute HNO_3 and 2 drops of water to the residue, boil and centrifuge. Remove the supernatant liquid to another tube. Repeat this treatment with HNO_3 and water and add to the liquid removed before. The sulfides of Pb, Bi, Cu, and Cd are dissolved. If Hg is present it remains as a residue.

Mercury: If a residue remains after the nitric acid treatment, add to it 1 drop of conc. HNO_3 and 3 drops of conc.

HCl. Boil until all Cl_2 is removed. Test a drop of the solution with $SnCl_2$-- a grey precipitate is a test for mercury. A confirmatory test may be made using Na_2CO_3 and diphenylcarbazide. A blue to violet color is a test for mercury. These tests for mercury are the same as those used in Group I. For more fully explained directions see page 13.

Lead: To the solution which may contain Pb, Bi, Cu and Cd, add 3 drops of conc. H_2SO_4. If a white precipitate ($PbSO_4$) forms at once, centrifuge and remove the supernatant liquid to another tube. If no precipitate forms, boil the liquid until white fumes of SO_3 are evolved. This should be done in a crucible. Then draw up the liquid into a pipette and drop it into a centrifuge tube containing 3 drops of water. (According to Engelder the precipitate forms only after SO_3 is boiled off and the solution added to water. But every time that I did the experiment I obtained a white precipitate immediately upon addition of the H_2SO_4.) A white precipitate is $PbSO_4$. Centrifuge and remove the supernatant liquid to another tube. Wash the white precipitate with 3 drops of water, centrifuge and add this liquid to that removed before. Dissolve the residue of $PbSO_4$ by adding 2 drops of ammonium acetate $NH_4(C_2H_3O_2)$ and heating. Then add 2 drops of K_2CrO_4 to the solution. The formation of a yellow precipitate is a good test for lead.

Bismuth: To the liquid which may contain Bi, Cu and Cd, add an excess of conc. NH_4OH, 5-10 drops. (Engelder says

until precipitation of $Bi(OH)_3$ is complete.) This should completely precipitate the bismuth as $Bi(OH)_3$ and there should be an excess of NH_4OH so that any $Cu(OH)_2$ or $Cd(OH)_2$ formed will be redissolved. (The hydroxides of Cu and Cd are soluble in excess NH_4OH.) If the solution is blue, it is a good indication of copper. Centrifuge and remove the supernatant liquid to another tube. Wash the residue with 2 drops of water and 2 drops of dilute NH_4OH. Centrifuge and add the supernatant liquid to that removed before. Place 2 drops of $SnCl_2$ in a cavity of the spot plate. Add NaOH to this until the precipitate which first forms is redissolved. Now add 2 drops of water to the residue of $Bi(OH)_3$ and stir. Take a drop of this mixture of precipitate and water and place it in the solution of Na_2SnO_2 on the spot plate. A black precipitate (metallic bismuth) is a test for bismuth. (Engelder does not add water to the residue of $Bi(OH)_3$ but places a very small piece of filter paper on the end of a platinum wire, dips it into the $Bi(OH)_3$ and then into the Na_2SnO_2. I could not obtain a good test in this manner.) (Two confirmatory tests are omitted. One used KI and CsCl. The other used I_2 cinchonine reagent.)

Copper: Place a drop of the solution which may contain Cu and Cd on the spot plate. As stated before if the solution is blue this is an indication of copper. Add dilute HCl until acid, then add a drop of potassium ferrocyanide, $K_4Fe(CN)_6$. A reddish brown precipitate is a test for copper. (Two confirmatory tests were omitted.)

Cadmium: If copper has been shown to be present add KCN (Poison) drop by drop to the remainder of the solution until the blue color disappears. Then pass in H_2S. A yellow precipitate (CdS) shows the presence of cadmium. In the absence of copper make the solution just acid with dilute H_2SO_4 and then pass in H_2S. (Engelder does not add H_2SO_4 but I obtained no precipitate without it.) A yellow precipitate is a test for cadmium. In either case if a dark precipitate is obtained, add a few drops of 1-4 H_2SO_4 (mix 1 drop of H_2SO_4 with 4 drops of water on a spot plate). Warm and centrifuge. Remove the supernatant liquid and neutralize with NH_4OH. Then add 1 drop of dilute H_2SO_4 and pass in H_2S. If cadmium is present a yellow precipitate will form.

Division B. To the solution extracted by the Na_2S treatment add dilute HCl drop by drop until just acid. Precipitation should begin when solution is just acid, but As, Sb and Sn do not precipitate at once. Orange Sb_2S_3 comes down first, then yellow As_2S_3 and finally SnS. Therefore several drops more of HCl will probably have to be added for complete precipitation, even after solution has been made just acid; however too much HCl should not be added as this causes precipitation of free sulfur--this till be seen as a white precipitate. (Engelder says to make just acid.) Centrifuge. The supernatant liquid may be turbid due to free sulfur. Discard this liquid. Wash the residue of sulfides twice with water discarding the supernatant liquid. (This was not done in

Engelder's scheme.) Add 3 drops of conc. HCl to the residue, boil, add 2 drops of water. Centrifuge and remove the supernatant liquid. This may be Sb and Sn. The residue may be As_2S_5 and possibly a trace of HgS. Wash the residue with water until only faintly acid. The first washing is added to the solutions Sb and Sn previously removed. Other washings are discarded.

Arsenic: Add 4 drops of dilute NH_4OH to the residue and heat. Centrifuge and remove the liquid. Repeat this extraction with 2 drops of dilute NH_4OH. Add the liquid removed before. Repeat this extraction discarding the liquid until a drop of the liquid when tested with dilute does not give a yellow precipitate. If a black residue remains treat with aqua regia and test for mercury as in Group I, page 12. To the combined extracts of As, add dilute HCl until acid. Centrifuge. A yellow precipitate which is insoluble in conc. HCl is a good indication of arsenic. (Tried to obtain $MgNH_4AsO_4$ as a test, but could not get it. Also tried the test with $AgNO_3$ to get a chocolate brown precipitate, but did not get this test either.)

The tests for Sb and Sn are made without separation of the Sb-Sn liquid.

Antimony: Place a drop of solution on a spot plate. Pass H_2S into the drop. A bright orange precipitate is an indication of antimony. If the test is negative add a drop of water and again pass in H_2S. Place another drop of solution

on the spot plate. In this place a very small piece of tin. A blackening of the tin confirms the presence of antimony. (Not used by Engelder.)

Tin: Place a drop of Sb-Sn solution on a spot plate. Add a drop of NH_4MoO_4 solution. A dark blue precipitate is a test for tin. (Not used by Engelder.) To the rest of the solution add some iron powder or a small iron nail. Boil 2-3 minutes. This reduces tin to stannous form. Centrifuge and place a drop of the supernatant liquid on a glass slide. Add a drop of $HgCl_2$. A white or grey precipitate is a test for tin. (Not used by Engelder. Engelder uses a test for Sn with rhodamine B solution, and another with cacothelone solution. He also gives a test in which the bottom of a crucible is immersed in the solution to which has been added some granulated zinc. The crucible is held in a flame and a blue color should be seen. Due to the blue color of the flame used, or because the test did not work, no test was obtained. CsCl is also used to test for both Sn and Sb by Engelder.)

Group III- Fe, Mn, Al, Cr, Ni, Co, Zn.

To a solution of Group II alone or to the liquid saved after removal of Group II, add a drop of NH_4Cl, then make alkaline with conc. NH_4OH (excess), stir and centrifuge. Fe, Mn, Al, and Cr are precipitated as hydroxides. Remove the supernatant liquid which may contain Ni, Co, Zn of Group III, as well as Groups IV and V. Save this liquid in a stoppered, labelled tube for further analysis. Wash the residue twice with 2 drops of conc. NH_4OH and 2 drops of water. Centrifuge and add these washings to the supernatant liquid previously removed.

To the residue add 3 drops of water, 3 drops of NaOH and carefully a little powdered Na_2O_2. When effervescence has ceased, centrifuge and transfer the supernatant liquid to another tube. The residue may be Fe and Mn. The liquid may be Cr and Al (yellow if Cr is present).

Wash the residue until only faintly basic (use 10 drops or more of water per washing). Discard all the washings. Then add 3 drops of dilute HNO_3 and 2 drops of H_2O_2 (3%) to the residue, and stir. If not completely soluble, add more H_2O_2.

Iron: Place a drop of the solution on a spot plate; add a drop of dilute HCl and a drop of potassium ferrocyanide $K_4Fe(CN)_6$. A precipitate of Prussian blue shows that iron is present. To another drop of the solution on a spot plate add a drop of sulfosalicylic acid, 10% solution. A red-blue color is a test for iron.

Manganese: To another drop of the solution on a spot plate add a drop of conc. HNO_3 and a little powdered sodium bismuthate ($NaBiO_3$). A purple color due to the MnO_4 ion identifies manganese. (Omitted a test using benzidine.)

Chromium: Place a drop of the solution containing Cr and Al (from the separation of Fe and Mn) on a spot plate. To this add a drop of saturated $Pb(C_2H_3O_2)_2$ solution. A yellow precipitate proves the presence of chromium. (Engelder uses powdered $Pb(C_2H_3O_2)_2$. But when you begin with a powder it is hard to see a precipitate form. Therefore a saturated solution is better.

Aluminum: To the remainder of the Cr-Al solution add dilute HNO_3 until acid. Add a little powdered $NH_4(C_2H_3O_2)$, 5 drops of aluminon and then carefully make just basic with NH_4OH. The formation of a "red lake" (red precipitate) proves the presence of aluminum.

Into the solution which contains the rest of Group III (Ni, Co and Zn) and may contain Groups IV and V, pass in H_2S, centrifuge and test for complete precipitation. After complete precipitation, centrifuge and remove the supernatant liquid (which may contain Groups IV and V) to another tube. Make this solution acid with $HC_2H_3O_2$ and then boil (in a micro casserole, if available) to expel the H_2S. If any precipitate is formed, centrifuge, remove the liquid and save for later analysis. Discard the residue. If Group II alone is being analyzed for, discard the liquid immediately after passing in the H_2S and

centrifuging. (Tried the borax bead test for cobalt, but could not obtain good results.)

The precipitate obtained by passing in H_2S may be the sulfides of Ni, Co and Zn. Add 5 drops of 1-9 HCl (made by mixing 1 drop of conc. HCl and 9 drops of water in a spot plate) to the residue. Stir, warm and centrifuge. The residue is Ni and Co. Remove the supernatant liquid which is $ZnCl_2$ to another tube.

Zinc: Place a drop of solution on a spot plate, add 1 drop of 1% $CuSO_4$ and 1 drop of $NH_4CNS.HgCl_2$ solution. A blue-black color indicates zinc. Neutralize the rest of the solution with dilute NH_4OH and pass in H_2S. A white precipitate is proof of zinc. If the precipitate is dark in color, make strongly basic with conc. NH_4OH, centrifuge, and remove the supernatant liquid to another tube. Discard any residue. Neutralize the liquid with conc. HCl, then make basic with NH_4OH and again pass in H_2S. If zinc is present a white precipitate forms.

Nickel: To the residue which may be Ni and Co, add 1 drop of conc. HNO_3 and 3 drops of conc. HCl and boil until all the chlorine is expelled,--testing with moist KI starch paper. (As before used aqua regia in place of $KClO_3$ and HCl.) Place a drop of the clear solution on a spot plate and add a drop of conc. NH_4OH, and a drop of dimethyl glyoxime. The formation of a red precipitate proves the presence of Ni.

Cobalt: Place another drop of the Ni-Co solution on

a spot plate. Neutralize with NH_4OH and then make acid with $HC_2H_3O_2$. Add a drop of alpha nitroso--beta naphthol solution. A red precipitate shows the presence of cobalt. Place another drop of solution on the spot plate and add 2-3 drops of H_2O_2, and then add a little powdered $NaHCO_3$. (Engelder calls for a crystal of $KHCO_3$. This was not in stock so used the $NaHCO_3$.) A green color shows the presence of cobalt. Place another drop of solution on the spot plate, add 2-3 drops of alcohol and a crystal of ammonium thiocyanate (NH_4SCN). A blue color identifies cobalt.

Group IV- Ca, Sr, Ba.

To a solution of Group IV alone, or to the liquid obtained after separation of Group II, add a little solid NH_4Cl. Make slightly basic with conc. NH_4OH and then add a solution of $(NH_4)_2CO_3$ drop by drop until precipitation is complete. Members of Group IV are precipitated as carbonates. Centrifuge and remove the supernatant liquid to another tube if Group V is to be analyzed for. Otherwise discard the liquid.

Dissolve the residue of carbonates by adding 1 or 2 drops of dilute HCl. Warm, and add 3 drops of water and then add dilute H_2SO_4 drop by drop until Sr and Ba are completely precipitated as sulfates. Centrifuge and add another drop of dilute H_2SO_4 to test for complete precipitation. Again centrifuge.

Calcium: Place 2 drops of the supernatant liquid on a glass slide, add a little solid NH_4Cl until saturated, and then add a drop of conc. $K_4Fe(CN)_6$. A white precipitate indicates calcium. Remove the rest of the supernatant liquid to another tube. Dip a platinum wire into the solution, then hold in a flame. A yellow-red colored flame is an indication of calcium. To the liquid containing calcium, add conc. NH_4OH until neutral, then acidify with 2 drops of $HC_2H_3O_2$. Add $(NH_4)_2CrO_4$ until precipitation is complete. A white precipitate is CaC_2O_4. Centrifuge and discard the supernatant liquid. Apply the flame test to the precipitate. A yellow-red flame shows that calcium is present.

Barium and Strontium: Dip a platinum wire into conc. HCl, heat in the oxidising flame and then dip the wire into the precipitate of Ba and Sr carbonates. Heat the wire from the middle towards the tip in the reducing zone of the flame. If any calcium was present, a yellow-red flash will appear first. The deep red flame of strontium appears immediately afterwards, and finally a pale green flame indicates barium. These appear in the order named due to different degrees of volatility.

Group V- NH_4 , Mg, K, Na.

Ammonium ion: This test is performed on the original sample. Place 2 drops of the solution in a 1 cc. tube. Add 2 drops of NaOH solution. Place a strip of moist neutral or red litmus paper over the mouth of the tube. Heat gently. A blue coloring of the litmus paper indicates the ammonium ion.

The following tests are carried out on the liquid saved from Group IV.

Magnesium: Place 2 drops of the solution in a micro crucible (or casserole), add 2 drops of NaOH and boil. This removes any ammonium ion which interferes with the test. Make up any decrease in volume with water. Place a drop of this solution on a spot plate. Add a drop of alkaline p-nitrobenzene-azoresorcinol. A blue precipitate shows the presence of magnesium. (Engelder does not take precaution to remove the NH_4 ion, and since NH_4Cl has been previously added, this always interferes with the test unless removed.)

Potassium: Place 3-4 drops of the liquid from Group IV in a micro crucible (or casserole). Acidify with dilute HNO_3. Evaporate to dryness, and continue heating until fumes are no longer evolved. Let cool, and add 2 drops of water. Warm solution. Place a drop of the solution on a glass slide; add a drop of saturated $Na_3Co(NO_2)_6$ solution. A yellow precipitate proves the presence of potassium. (A saturated solution of $Na_3Co(NO_2)_6$ is used in place of the powder which Engelder calls for. It is very hard to see a yellow precipi-

tate form when you begin with a yellow powder.) (The flame test for potassium was omitted.)

Sodium: Dip a platinum wire into the supernatant liquid from Group IV. Hold it in the Bunsenflame. A persistent yellow flame indicates sodium.

The Anion Analysis

The application of micro methods to anion analysis did not prove to be as satisfactory as in cation analysis. However it must be remembered that even in macroanalysis the scheme for the detection of anions is inferior to that for the detection of cations. The technique for the handling of micro quantities does not seem to be at fault. But the low concentration of the anion radicals seems to cause difficulty. Solutions containing not more than 1 mg. of any one anion per cc. were used.

The anions arrange themselves into four groups:

I. Those which evolve a gas upon the addition of dilute HCl.

II. Those which give a precipitate upon the addition of mixture of $BaCl_2$ and $CaCl_2$.

III. Those which give a precipitate with $AgNO_3$ when added to the solution acidified with nitric acid.

IV. Those anions, only two, not effected by the above reagents.

Only the more common anions and those easily detected are included in this scheme of anion analysis.

Group I- Nitrites, sulfides, sulfites, carbonates.

Test a drop of the solution with a drop of dilute HCl to determine if the group is present.

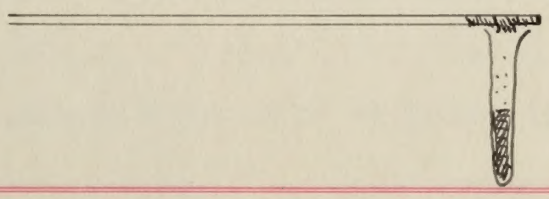
In the following tests in which a gas is evolved, the small test tubes used are those mentioned in the section on apparatus on page 9. Their capacity is from 5 to 8 drops. (Engelder does not use this apparatus.)

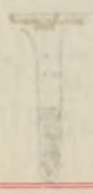
Nitrites: Place a drop of solution in a small test tube and add a drop of dilute H_2SO_4. Hold a strip of moistened potassium iodide starch paper above the mouth of the tube. Heat the tube gently. If nitrites are present the paper becomes colored dark blue. The gas evolved will appear brown.

Sulfides: Place a drop of solution in a small test tube, add a drop of dilute H_2SO_4. Hold a piece of moistened lead acetate paper above the mouth of the tube. Warm the tube. A blackening of the paper indicates the presence of sulfides. (A test using alpha amino-dimethyl-aniline is omitted.)

Sulfites: Place a drop of solution in a small test tube, add a drop of strontium nitrate solution. (Engelder used strontium acetate.) If a preceipitate forms, centrifuge and pipette off the supernatant liquid. Wash the residue with water. On a spot plate mix a drop of 1% $KMnO_4$ with 3 drops of water and 3 drops of dilute H_2SO_4. (Engelder says to use dilute $KMnO_4$ only.) Add a drop of this $KMnO_4$ solution to the residue in the test tube. A bleaching of the $KMnO_4$ shows the presence of sulfites.

Carbonates: The test for carbonates caused considerable trouble. CO_2 is evolved upon addition of dilute HCl and the gas tested with saturated $Ba(OH)_2$ solution. Engelder says to hold a drop of the $Ba(OH)_2$ in a loop of platinum wire. It was, however, difficult to obtain a good test in this manner. It was hard to get a drop to remain in the wire loop, and also hard to hold it steady so as not to touch the tube. Other methods were tried: a drop of $Ba(OH)_2$ was held on a glass rod; black filter paper was saturated with $Ba(OH)_2$ and held above the tube; a capillary tube to conduct the gas into a drop of $Ba(OH)_2$ was devised. All these methods did not appear satisfactory. As a matter of fact, the $Ba(OH)_2$ becomes milky when exposed to air in the laboratory without being exposed to CO_2 gas. Finally a tube 1 mm. in diameter was made and cut in 6 or 7 cm. lengths. One end of the tube was sealed. Then the sealed end was held in the flame while the person blew into the other end. This caused a small hole to be blown out on the side of the tube. This tube was dipped into the saturated solution of $Ba(OH)_2$ and then the outside of the tube wiped off. This tube was then held above the tube from which the CO_2 was being evolved in a manner such that the hole in the side of the tube containing the $Ba(OH)_2$ was just above the mouth of the tube containing the solution. The test was satisfactory with this apparatus.





If sulfites have been shown to be present add a drop of H_2O_2 (3%) to a drop of the solution. Then add a drop of dilute HCl and test the gas evolved with saturated $Ba(OH)_2$ solution, held in the tube described above. This test worked well.

Cyanides and thiosulfates are also members of Group I included by Engelder, but here omitted.

Group II- Phosphates, chromates, sulfates, borates, tartrates.

Test a drop of solution with a mixture of $BaCl_2$ and $CaCl_2$ solution. A precipitate shows that Group II is present.

Phosphates: Cut a small strip of filter paper. On a spot plate make a saturated solution of $Na_2B_4O_7$. Also make a sulfuric acid solution of $(NH_4)MoO_4$. Dip the filter paper first into the solution to be tested and then into the solution of sodium borate. Then treat the paper with a solution of $SnCl_2$ (20%) and finally a drop of the sulfuric acid solution of $(NH_4)MoO_4$. Dry the filter paper over a flame. A blue color is due to either phosphates or arsenates. Place the paper on a spot plate and treat with ether. If the color is due to phosphates it will disappear with the ether treatment. (Engelder also uses the test with magnesia mixture. However I could obtain no white precipitate with this reagent.)

Chromates: Place 2-3 drops of the solution to be tested in a small centrifuge tube. Acidify with conc. HNO_3 and add 3-5 drops of ether. Then add 3 drops of 3% H_2O_2. A blue color proves the presence of chromates. This blue color should be in the ether layer, but seemed to be just as noticeable throughout the solution. (Engelder says the blue color is in the ether layer. He also says that a yellow colored solution (original) is a good indication of chromates. But a solution of 1 mg. per cc. of the anion is not perceptibly yellow.)

Sulfates: Place 2 drops of solution in a centrifuge

tube and add 2 drops of $BaCl_2$ solution. Centrifuge and remove the supernatant liquid. Add a drop of conc. HCl. If the white precipitate (or part of it) is insoluble in conc. HCl this indicates sulfates. Wash the residue twice with hot water. Add a drop of $Hg(NO_3)_2$ to the residue and warm. A yellow color on the surface of the residue shows the presence of sulfates. If the color is not apparent add 2-3 drops of water, stir and again warm. A yellow color throughout the solution indicates sulfates. (The underlined is not included by Engelder.)

Borates: To a drop of solution add a drop of dilute HCl. Moisten a strip of tumeric paper with this solution. Dry the paper over a flame. Add a drop of 1% NaOH to the paper. A reddish brown or pink color indicates borates. (Engelder says a light blue or reddish brown color.) Engelder also includes another test for borates in which a drop of solution is placed in a micro crucible, a drop of conc. H_2SO_4 added and finally several drops of alcohol are added. This is ignited and the flame shows the presence of borates if it is colored green. There may have been a flash of green at the edge of the flame when first ignited, but for the concentration of the solution used, I did not consider the test a good one.

Tartrates: Wash out one of the tubes used for gas analysis in Group I with NaOH. Place a drop of the solution in this tube. Add a drop of $AgNO_3$ solution and a drop of NaOH. Then add dilute NH_4OH (1 or 2 drops) until any precipitate formed has disappeared. Warm gently. The formation of a silver

mirror proves the presence of tartrates. If the mirror does not form, set the tube aside for some time. The mirror may be slow in forming.

(Engelder also includes arsenites, arsenates, silicates, fluorides and oxalates in this group.)

Group III- Ferricyanides, ferrocyanides, iodides, bromides, chlorides.

To a drop of solution add a drop of dilute HNO_3 and a drop of $AgNO_3$. A precipitate indicates Group III.

Ferricyanides: Place a drop of solution on a spot plate, acidify with dilute HCl, add a drop of freshly prepared $FeSO_4$ solution. A blue precipitate, Turnball's blue, indicates the presence of ferricyanides.

Ferrocyanides: Place a drop of solution on a spot plate, acidify with dilute HCl, add a drop of $FeCl_3$ solution. A deep blue precipitate, Prussian blue, indicates the presence of ferrocyanides.

Iodides: Place a drop of solution in a centrifuge tube, acidify with a drop of dilute HCl and add 3 drops of chloroform. Then add a solution of sodium hypochlorite drop by drop. If the chloroform layer becomes violet iodides are present. This test is very sensitive.

Bromides: Place a drop of solution in a centrifuge tube, acidify with a drop of dilute HCl and add 3 drops of chloroform. Then add a solution of sodium hypochlorite drop by drop. A brown color in the chloroform layer indicates bromides.

If iodides are present, I_2 will be extracted first. Engelder says to add NaOCl solution until the solution becomes colorless, and then add dilute H_2SO_4 to obtain the brown color for bromides. This however did not work well, and no satis-

factory test was found for testing for bromides in the presence of iodides.

Chlorides: If I^- and Br^- are known to be absent, add a drop of $AgNO_3$ solution to a drop of the unknown on a glass slide. Acidify with dilute HNO_3. A white precipitate which dissolves in conc. NH_4OH shows the presence of chlorides.

In the presence of I^- and Br^- acidify 2 drops of solution with acetic acid. Add a little PbO_2 and boil to remove I_2 and Br_2. Cool and centrifuge. Test a drop of the clear supernatant liquid, on a glass slide, by acidifying with a drop of $AgNO_3$. A white precipitate indicates chlorides. If the precipitate should be yellow-white, this indicates that either I_2 or Br_2 have not been completely removed. In which case, boil again and repeat the test.

Engelder does not mention the fact that cyanogen ions should be removed before the tests for the halides. The method for separation used in the macro scheme is not applicable to micro methods, except with difficulty; and I have not worked out a plan for separation.

Engelder includes the cyanates in this group.

Group IV- Nitrates, acetates.

Nitrates: To remove interfering substances, add to 3 drops of solution in a centrifuge tube, 2-3 drops of saturated Ag_2SO_4 solution. Test for complete precipitation. Centrifuge. Place a drop of the supernatant liquid on a spot plate. In this drop place a small crystal of $FeS6_4.7H_2O$. Finally add a drop of conc. H_2SO_4. A brown ring around the crystal indicates nitrates. This test can also be carried out in one of the small test tubes used in Group I. A drop of saturated $FeSO_4$ solution is first placed in the tube, then a drop of the solution to be tested, and finally a drop of conc. H_2SO_4 is allowed to run down the side of the tube. A brown ring above the $FeSO_4$ layer is an indication of nitrates.

Acetates: Place a drop of unknown solution in a crucible, add 2 drops of ethyl alcohol and 5 drops of conc. H_2SO_4. Warm gently. A fruity odor indicates acetates. This was not a good test, as the odor is barely perceptible.

A test with lanthanum nitrate was tried but gave poor results.

Conclusion

After having worked over the scheme of microanalysis outlined by Engelder, I am convinced that the method is a practical one, which can be used successfully in qualitative analysis courses for the general student. Complex unknowns have been correctly analyzed by these micro methods. It must be admitted that the amalysis for anions is not quite as good as that for cations, but I think this is true of any scheme in qualitative analysis.

Microanalysis is more than a practical course; I think it has several advantages over the macroanalysis generally used. The micro method makes possible an economy in material, space and time. A class in qualitative analysis using micro methods will use considerably less materials than if they employed macro methods. The small amounts of substances used, will in turn require smaller stock room space. Not only this but the individual students will need but very little space in which to keep their apparatus. The only general apparatus used by the whole class will be the centrifuge and a hydrogen sulfide generator. A large class will require several centrifuges. There is economy in materials, space and finally in time. Microanalysis is a shorter method because all the long filtrations have been replaced by the short method of centrifuging. The time necessary for heating and evaporating are also shortened. Some of the time saved in the analysis will be required for making apparatus. In the macro method, the

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student has no apparatus to make, but when using micro apparatus it is generally necessary for the individual student to make much of his own apparatus. Even deducting the time needed for making apparatus, however, there is a saving of time.

I consider it an advantage for the student to have to make his own apparatus. The process is very simple, but gives the student practice and skill in manipulating glass for making this apparatus. Micro methods, in general, are particularly valueable to the student in developing in him a more careful, neat and exact technique than are obtained when using macro methods.

Microanalysis is therefore to be recommended as a practical method which makes possible a saving in materials, space and time, and is very beneficial to the student because it teaches him a technique which demands care, neatness and exactness.

REAGENTS

Aluminon--$C_{19}H_9O_2(COONH_4)_3$--0.1% solution in water. (for Aluminum)

Dimethyl-glyoxime--$C_4H_8N_2O_2$--1 gm. in 100 c.c. 95% alcohol. (for Nickel)

Diphenyl Carbazide--saturated alcohol solution. (for Mercury) J.A.C.S. 51, 3351.

Para-nitrobenzene-azoresorcinol--$C_{12}H_9N_3O_4$--0.001 gm. of reagent in 100 c.c. 2 N NaOH. (for Magnesium)

Alpha-nitroso-beta-naphthol--$C_{10}H_6OH(NO)$--saturated solution in 50% acetic acid. (for Cobalt)

Ammonium thiocyanate-mercuric thiocyanate--2 $NH_4CNS.Hg(CNS)_2$--dissolve 60 gm. of $HgCl_2$ and 66 gm. of NH_4CNS in 100 cc. of water. (for Zinc)

SOLUTIONS

The stock solutions were made up to contain 10 milligrams of metallic ion per cubic centimeter. The test solutions were made up using 1 c.c. of each solution and making it up to a final volume of 10 c.c. so that this test solution contained 1 mg. per c.c. of each cation. This is one tenth the concentration used in macro work.

CATIONS

Constituent	Formula	Grams/100 c.c.
Silver	$AgNO_3$	1.6
Lead	$Pb(NO_3)_2$	1.6
Mercury (ous)	$Hg_2(NO_3)_2.2H_2O$	1.4 (Dissolve in 6 N HNO_3)
Mercury (ic)	$HgCl_2$	1.4
Bismuth	$Bi(NO_3)_3.5H_2O$	2.3 (Dissolve in 3 N HNO_3)
Copper	$Cu(NO_3)_2.3H_2O$	3.8
Cadmium	$Cd(NO_3)_2.4H_2O$	2.7
Arsenic	As_2O_5	1.5
Antimony	$SbCl_3$	1.9 (Dissolve in 6 N HCl)
Tin	$SnCl_4.3H_2O$	2.7 (Dissolve in 6 N HCl)
Aluminum	$Al(NO_3)_3.9H_2O$	14.0
Zinc	$Zn(NO_3)_2$	2.9
Chromium	$Cr(NO_3)_3$	4.6
Iron	$FeCl_3$	3.0
Manganese	$Mn(NO_3)_2.6H_2O$	5.3
Nickel	$Ni(NO_3)_2.6H_2O$	5.0
Cobalt	$Co(NO_3)_2.6H_2O$	5.0

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Mercury (ous)	$Hg_2(NO_3)_2.2H_2O$	1.4 (Dissolve in 6 N HNO_3)
Mercury (ic)	$HgCl_2$	1.4
Bismuth	$Bi(NO_3)_3.5H_2O$	2.3 (Dissolve in 3 N HNO_3)
Copper	$Cu(NO_3)_2.3H_2O$	3.8
Cadmium	$Cd(NO_3)_2.4H_2O$	2.7
Arsenic	As_2O_3	1.8
Antimony	$SbCl_3$	1.9 (Dissolve in 6 N HCl)
Tin	$SnCl_4.3H_2O$	2.7 (Dissolve in 6 N HCl)
Aluminum	$Al(NO_3)_3.9H_2O$	14.0
Zinc	$Zn(NO_3)_2$	2.9
Chromium	$Cr(NO_3)_3$	4.6
Iron	$FeCl_3$	3.0
Manganese	$Mn(NO_3)_2.6H_2O$	5.3
Nickel	$Ni(NO_3)_2.6H_2O$	5.0
Cobalt	$Co(NO_3)_2.6H_2O$	5.0

Barium	$BaCl_2.2H_2O$	1.8
Strontium	$Sr(NO_3)_2$	2.4
Calcium	$Ca(NO_3)_2.4H_2O$	5.9
Magnesium	$Mg(NO_3)_2.6H_2O$	10.6
Sodium	$NaNO_3$	3.7
Potassium	KNO_3	2.6

ANIONS

Constituent	Formula	Grams/100 c.c.
Sulfide	$Na_2S.9H_2O$	7.5
Iodide	KI	1.3
Chloride	NaCl	1.65
Sulfate	$Na_2SO_4.10H_2O$	3.4
Sulfite	$Na_2SO_3.7H_2O$	3.15
Nitrate	$NaNO_3$	1.4
Nitrite	$NaNO_2$	1.5
Borate	$Na_2B_4O_7.10H_2O$	0.9
Carbonate	Na_2CO_3	1.7
Phosphate	$Na_2HPO_4.12H_2O$	3.8
Chromate	K_2CrO_4	1.7
Ferricyanide	$K_4Fe(CN)_6.3H_2O$	2.1
Ferrocyanide	$K_3Fe(CN)_6$	1.5
Acetate	$Na(C_2H_3O_2)$	1.25
Tartrate	$C_4H_6O_6$	1.00

Barium	$BaCl_2 \cdot 2H_2O$	1.8
Strontium	$Sr(NO_3)_2$	2.4
Calcium	$Ca(NO_3)_2 \cdot 4H_2O$	5.9
Magnesium	$Mg(NO_3)_2 \cdot 6H_2O$	10.6
Sodium	$NaNO_3$	3.7
Potassium	KNO_3	2.6

ANIONS

Constituent	Formula	Grams/100 c.c.
Sulfide	$Na_2S \cdot 9H_2O$	7.5
Iodide	KI	1.3
Chloride	NaCl	1.65
Sulfate	$Na_2SO_4 \cdot 10H_2O$	3.4
Sulfite	$Na_2SO_3 \cdot 7H_2O$	3.15
Nitrate	$NaNO_3$	1.4
Nitrite	$NaNO_2$	1.5
Borate	$Na_2B_4O_7 \cdot 10H_2O$	0.9
Carbonate	Na_2CO_3	1.7
Phosphate	$Na_2HPO_4 \cdot 12H_2O$	3.8
Chromate	K_2CrO_4	1.7
Ferricyanide	$K_3Fe(CN)_6 \cdot 3H_2O$	2.1
Ferrocyanide	$K_4Fe(CN)_6$	1.5
Acetate	$Na(C_2H_3O_2)$	1.25
Tartrate	$C_4H_6O_6$	1.00

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